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(54) Photocurable composition

(57) A photocurable composition useful for the preparation of printed wiring boards which includes
(a) 20-50 parts by weight of a modified rosin;
(b) 20-40 parts by weight of a first acrylic derivative expressed by the following formula:
$HOOC\text{-}Y\text{-}COO\text{-}CH_2CH_2OCO\text{-}CCH_3{=}CH_2$
wherein Y stands for 1,2-cyclohexylene;
(c) 5-35 parts by weight of a second acrylic derivative selected from hydroxyalkyl acrylates and hydroxyalkyl methacrylates;
(d) 10-40 parts by weight of a monomer other than (b) and (c) and having one ethylenically unsaturated group;
(e) 0.5-15 parts by weight of a photopolymerization initiator; and
(f) 0.5-10 parts by weight of a montmorillonite organic complex.
The composition has good reproducibility and on exposure, the uncured areas are easily removable and the cured areas are resistant to chemicals such as etchants.

PHOTOCURABLE, RESIST INK COMPOSITION

Background of the Invention

This invention relates generally to a photocurable composition and, more specifically, to a resist ink useful in fabrication of printed wiring boards for forming, by screen printing, a wiring pattern which is curable by irradiation of UV rays and which becomes, upon curing, resistive against attack by chemicals such as an electroplating solution and an etching solution.

A method for the fabrication of printed wiring boards is known which includes the steps of screen printing of a resist ink on a board, curing of the printed ink by irradiation of UV rays, chemical etching with, for example, an aqueous ferric chloride or cupric chloride solution, and removing of the cured resin on the board using, for example, an aqueous caustic soda. Another known method includes the steps of screen printing of a resist ink on a board, curing of the printed ink by irradiation of UV rays, electroplating with the use of, for example, cupric sulfate, and removing of the cured resin using, for example, an aqueous caustic soda.

The UV-curable resist ink to be used in the above methods should meet with the following criteria:

(1) the ink should afford uniform wiring patterns with good reproducibility by screen printing;

(2) the cured ink should withstand chemical attack during the etching and electroplating steps; and

(3) the cured ink should be easily removable, generally by dissolution, during the removal step.

Known resist inks are, however, not fully satisfactory in this regard.

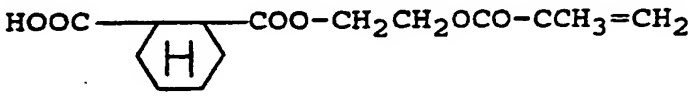
Brief Summary of the Invention

It is, therefore, the prime object of the present invention to provide a resist ink composition which satisfies all of the above conditions.

In accordance with the present invention there is provided a photocurable composition comprising the following ingredients (a)-(f):

(a) 20-50% by weight of a modified rosin;

(b) 20-40% by weight of a first acrylic derivative expressed by the following formula:



(c) 5-35% by weight of a second acrylic derivative selected from the group consisting of hydroxyalkyl acrylates and hydroxyalkyl methacrylates;

(d) 10-40% by weight of a monomer other than said first and second acrylic derivatives and having one ethylenically unsaturated group;

(e) 0.5-15% by weight of a photopolymerization initiator; and

(f) 0.5-10% by weight of a montmorillonite organic complex.

Other objects, features and advantages of the present invention will become apparent from the detailed description of the invention to follow.

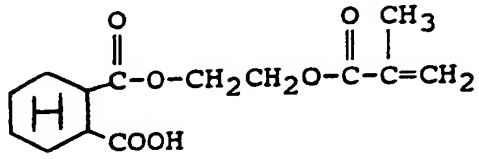
Detailed Description of the Invention

Details of the ingredients (a)-(f) constituting the photocurable ink composition according to the present invention will be explained below.

The modified rosin to be used as the ingredient (a) is preferably one modified with an acid or an

alcohol, such as maleic acid, fumaric acid, maleic anhydride, pentaerythritol or glycerin. It is preferred that the modified rosin have an acid value of 70-300. When the acid value is lower than 70, it takes a relatively long time to dissolve a cured layer of the resist ink composition in an aqueous alkali during the removing step. Too large an acid value of the modified rosin in excess of 300 tends to cause brittleness of the cured layer. The modified rosin should be used in an amount of 20-50% by weight based on the total weight of the ingredients (a)-(f). An amount of the modified rosin below 20% by weight is disadvantageous because a long time is required for removing a cured layer of the resist ink composition by dissolution in an aqueous alkali. On the other hand, when the amount of the modified rosin exceeds 50% by weight, the resulting composition becomes too viscous to print wiring patterns with good reproducibility.

The first acrylic derivative to be used as the ingredient (b) is monomethacryloyloxyethyl hexahydrophthalate (methacryloylethyl hydrogen hexahydrophthalate) of the formula:

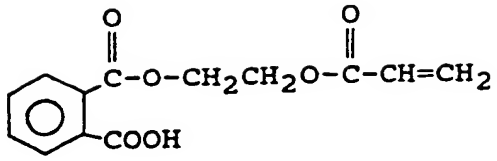


This compound may be obtained by reaction of hexahydrophthalic anhydride with 2-hydroxyethyl methacrylate. The first acrylic derivative should be used in an amount of 20-40% by weight based on the total weight of the ingredients (a)-(f). When the amount of the first acrylic derivative is lower than 20% by weight, it takes a long time to dissolve a cured layer of the resist ink composition in an aqueous alkali during the

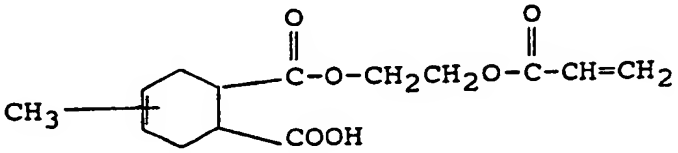
removing step. Too large an amount of the first acrylic derivative in excess of 40% by weight tends to cause brittleness of the cured layer.

The second acrylic derivative to be used as the ingredient (c) is a hydroxyalkyl acrylate or an hydroxyalkyl methacrylate. Illustrative of suitable acrylates and methacrylates are 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate. The compounds may be used by themselves or as a mixture of two or more. The amount of the second acrylic derivative should be 5-35% by weight based on the total weight of ingredients (a)-(d). An amount of the second acrylic derivative below 5% by weight is disadvantageous because the hydrophilicity of a cured layer of the resist ink composition becomes worth and because a long time is required for removing the cured layer by dissolution in an aqueous alkali. Too large an amount of the second acrylic derivative in excess of 35% by weight is disadvantageous because the hydrophilicity of the cured layer becomes so strong that resistance to etching solutions or to electroplating solutions becomes poor.

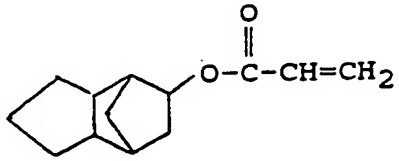
The monomer to be used as the ingredient (d) is a compound other than the above first and second acrylic derivatives and having only one ethylenically unsaturated group. Illustrative of suitable monomers are polycaprolactone monoacrylate, ethylene glycol monoethyl ether acrylate, ethylene glycol monoethyl ether acrylate, ethylene glycol monobutyl acrylate, diethylene glycol monomethyl ether acrylate, diethylene glycol monobutyl ether acrylate, phenyl glycidyl ether acrylate, phenoxyethyl acrylate, phenoxypropyl acrylate, phenoxypolyethylene glycol acrylate, phenoxypolypropylene glycol acrylate, monoacryloyloxyethyl phthalate of the formula:



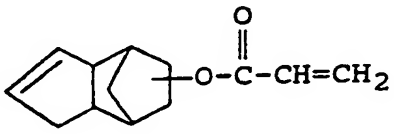
monoacryloyloxypropyl phthalate, monoacryloyloxyethyl tetrahydromethylphthalate of the formula:



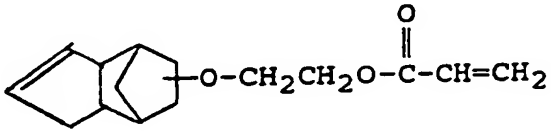
monoacryloyloxypropyl tetrahydromethylphthalate, dicyclopentanyl acrylate of the formula:



dicyclopentenyl acrylate of the formula:



dicyclopentenyl acrylate modified with ethylene oxide of the formula:



isobornyl acrylate, monoacryloyloxyethyl phosphate, polycaprolactone monomethyacrylate, ethylene glycol

monomethyl ether methacrylate, ethylene glycol monoethyl ether methacrylate, ethylene glycol monobutyl methacrylate, diethylene glycol monomethyl ether methacrylate, diethylene glycol monoethyl ether methacrylate, diethylene glycol monobutyl ether methacrylate, phenyl glycidyl ether methacrylate, phenoxyethyl methacrylate, phenoxypropyl methacrylate, phenoxypolyethylene glycol methacrylate, phenoxypolypropylene glycol methacrylate, monomethacryloyloxyethyl phthalate, monomethacryloyloxypropyl phthalate, monomethacryloyloxyethyl tetrahydromethylphthalate, monomethacryloyloxypropyl tetrahydromethylphthalate, dicyclopentanyl methacrylate, dicyclopentenyl methacrylate, dicyclopentenyl methacrylate modified with ethylene oxide, isobornyl methacrylate and monomethacryloyloxyethyl phosphate. These compounds may be used by themselves or as a mixture of two or more.

The monomer should be used in an amount of 10-40% by weight based on the total of the ingredients (a)-(f). An amount of the monomer below 10% by weight is disadvantageous because the hydrophilicity of the cured layer becomes so strong that resistance to etching solutions or to electroplating solutions becomes poor. On the other hand, when the amount of the monomer exceeds 40% by weight, the resulting composition becomes too low in viscosity to effect the printing of wiring patterns with good reproducibility.

The photopolymerization initiator to be used as the ingredient (e) may be, for example, benzoin alkyl ethers such as benzoin propyl ether, benzoin isopropyl ether, benzoin butyl ether and benzoin isobutyl ether; acetophenone compounds such as 2,2-diethoxyacetophenone and 2,2-dichloro-4-phenoxyacetophenone; propiophenone compounds such as 2-hydroxy-2-methylpropiophenone and 4-isopropyl-2-hydroxy-2-methylpropiophenone; anthraquinone compounds such as 2-ethylanthraquinone,

2-tert-butylanthraquinone, 2-chloro-anthraquinone; thioxanthone and substituted thioxanthones such as 2-chlorothioxanthone and 2,4-diethylthioxanthone; dibenzyl dimethyl ketal; 1-hydroxycyclohexyl phenyl ketone; and 2-hydroxy-2-methyl-1-phenylpropane-1-one. These initiators may be used by themselves or as a mixture of two or more thereof. Further, these initiators may be used in conjunction with an aminoalkyl benzoate such as ethyl p-dimethylaminobenzoate, isoamyl p-dimethylaminobenzoate or an amine such as methyldiethanol amine.

It is preferable to use, as the photopolymerization initiator, a mixture of a benzoin compound of the following formula (I) with a propiophenone compound of the following formula (II):

$$C_6H_5COCH(OR^1)C_6H_5 \qquad (I)$$

$$R^2\text{-}Z\text{-}COC(CH_3)_2OH \qquad (II)$$

wherein R^1 and R^2, independently from each other, stand for hydrogen or an alkyl and Z stands for 1,4-phenylene. The cojoint use of these compounds (I) and (II) can improve the photosensitivity of the ink, the hardness of the cured layer and the adhesion of the printed pattern on a board. Preferably, the symbol R^1 of the compound (I) is hydrogen or an alkyl having 1-4 carbon atoms such as methyl, ethyl, n-propyl i-propyl or n-butyl and the symbol R^2 of the compound (II) is hydrogen or an alkyl having 1-12 carbon atoms such as methyl, ethyl, n-propyl, isopropyl or n-hexyl.

The photopolymerization initiator should be used in an amount of 0.5 to 15% by weight based on the total of the ingredients (a)-(f). An amount of the initiator below 0.5% by weight is insufficient to effect the curing in a satisfactory rate. On the other hand, when the initiator is used in an amount of more than 15%

by weight, a cured layer of the resulting ink becomes so soft that it is easily injured.

The montmorillonite organic complex to be used as the ingredient (f) is a montmorillonite having its exchangeable cation ion-exchanged with an organic cation such as an alkyl ammonium or the formula $(R^1)_nN(R^2)_m$ wherein R^1 is hydrogen or a lower alkyl, R^2 is a higher alkyl having 8-20 carbon atoms, n is an integer of 2 or 3, m is an integer providing m+n of 4. The lower alkyl preferably has 1-3 carbon atoms and the higher alkyl preferably has 14-18 carbon atoms. A bentonite sol treated with dimethyl tallow alkyl ammonium chloride or trimethyl tallow alkyl ammonium chloride is particularly preferably used. Such a montmorillonite organic complex may be commercially available as Esben (Hojun Yoko K. K.), New Olben (Shiraishi Kogyo K. K.) or Olben M (Shiraishi Kogyo K. K.). The amount of the ingredient (f) should be 0.5 to 10% by weight based on the total of the ingredients (a)-(f). An amount of the montmorillonite organic complex outside of the above range fails to provide printed patterns with good reproducibility because of insufficient or excessive thixotropy of the resulting ink.

Preferred amounts of the ingredients (a)-(f) based on the total weight of the ingredients (a)-(f) are as follows:

(a) 22-45% by weight;
(b) 22-35% by weight;
(c) 10-30% by weight;
(d) 12-35% by weight;
(e) 1-10% by weight; and
(f) 1-8% by weight.

The photocurable ink composition of the present invention may contain a variety of conventional additives such as a polymerization inhibitor (e.g. methoquinone, BHT, kupferron), a pigment (e.g. Cyanin Blue, Carbon

Black, Cyanin Green), a filler (e.g. silica, barium sulfate, calcium carbonate, aluminum hydroxide, talc), a thixotropic agent (e.g. fine powder of anhydrous silica), an anti-foaming agent (e.g. silicone oil) or a surfactant (a nonionic surfactant).

The ink composition may be prepared in any known manner. For example, a mixture containing the ingredients (b), (c) and (d) is stirred by means of a dissolver at a temperature sufficient to melt the mixture, to which the ingredient (a) is added for dissolution therein. After the resulting mixture has been cooled to room temperature, the ingredient (e) is dissolved therein and, thereafter, the ingredient (f) is added. The mixture is homogeneously commingled by means of a three-roll mill, a ball mill or a sand mill to obtain the ink.

The following examples will further illustrate the present invention.

Examples 1 and 2 and Comparative Examples 1-3:

Resist inks having the compositions shown in Table 1 were prepared. In Table 1, the amounts are parts by weight. The performances of each of the inks were tested by the following methods and the results are summarized in Table 1.

Pattern Reproducibility

Using each of the inks, screen printing is performed with 300 mesh Tetlon, an emulsion thickness of 6 μm and a line and space of 150 μm. The printed pattern is then placed on a belt conveyor and passed beneath two 80 W/cm high pressure UV lamps at a distance of 17 cm and a belt speed of 4 m/min, thereby to cure the pattern. The line width of the cured pattern is measured for the evaluation of the pattern

reproducibility. The pattern reproducibility is rated as follows:

good: the line width is in the range of 135-165 μm

poor: the line width is outside of the 135-165 μm range

Resistance to chemicals

Cured patterns are produced in the same manner as in the above test. The pattern is subjected to etching at 40°C for 60 seconds at a spray pressure of 1.5 kg/cm^2 using an aqueous cupric chloride solution as an etching solution. The line widths D_0 and D_e before and after the etching, respectively, are measured to evaluate resistance to chemicals. The resistance is rated as follows:

good: D_e/D_0 is 0.95 to 1.0

poor: D_e/D_0 is below 0.95

Removability

Cured patterns are produced in the same manner as in the above tests. The pattern is immersed in a 3% by weight aqueous solution of sodium hydroxide and stirred at 40°C. The period of time required to dissolve the cured pattern is measured for the evaluation of the removability. The removability is rated as follows:

good: within 10 seconds

poor: more than 10 seconds

Table 1

Example No.	Ex. 1	Ex. 2	Comp. 1	Comp. 2	Comp. 3
Ingredient (a)					
Maleic acid-modified rosin *1	0	35	35	0	0
Maleic acid-modified rosin *2	30	0	0	30	30
Ingredient (b) *3	30	20	15	30	30
Ingredient (c)					
2-Hydroxyethyl acrylate	10	20	40	10	10
Ingredient (d)					
Diethylene glycol monoethyl ether acrylate	22	0	0	10	22
Phenoxyethyl acrylate	0	15	0	0	0
Ingredient (e)					
2,4-Diethylthioxanthone	2	0	0	2	2
Isoamyl p-dimethylaminobenzoate	4	0	0	4	4
Benzoin isopropyl ether	0	5	5	0	0
Ingredient (f)					
Bentonite organic complex *4	2	5	5	2	0
Cyanine Blue	1	1	1	1	1
Calcium carbonate	20	0	0	20	30
Diethylene glycol diacrylate	0	0	0	12	0
Test Result					
Pattern reproducibility	good	good	good	good	poor
Resistance to chemicals	good	good	poor	good	good
Removability	good	good	good	poor	good

Remarks:

*1: Beccasite J-892, manufactured by Dainihon Ink Kagaku Kogyo K. K.

*2: Markeed 3002, manufactured by Arakawa Kagaku Kogyo K. K.

*3: Monoethacryloyloxyethyl hexahydrophthalate, manufactured by Mitsubishi Rayon K. K.

*4: Bentonite sol ion-exchanged with trimethyl tallow alkyl ammonium ion, Orben M, manufactured by Shiraishi Kogyo K. K.

Example 3:

Example 2 was repeated in the same manner as described except that a mixture of 5 parts by weight of benzoin isopropyl ether and 4 parts by weight of 2-hydroxy-2-propiophenone were used as the ingredient (e). The cured pattern was found to exhibit better adherence and a higher pencile hardness as compared with that of Example 2. Further, the curing was able to be completed with a higher belt speed than that in Example 2.

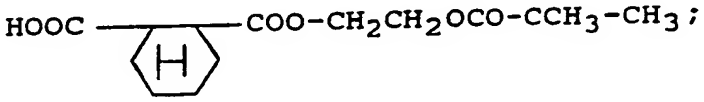
The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all the changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

CLAIMS:

1. A photocurable composition comprising the following ingredients (a)-(f):

(a) 20-50 parts by weight of a modified rosin;

(b) 20-40 parts by weight of a first acrylic derivative expressed by the following formula:



(c) 5-35 parts by weight of a second acrylic derivative selected from the group consisting of hydroxyalkyl acrylates and hydroxyalkyl methacrylates;

(d) 10-40 parts by weight of a monomer other than said first and second acrylic derivatives and having one ethylenically unsaturated group;

(e) 0.5-15 parts by weight of a photopolymerization initiator; and

(f) 0.5-10 parts by weight of a montmorillonite organic complex.

2. A composition as claimed in Claim 1, wherein said modified rosin has an acid value of 70-300.

3. A composition as claimed in Claim 1, wherein said modified rosin is a rosin modified with an acid or an alcohol.

4. A composition as claimed in Claim 1, wherein said second acrylic derivative is a member selected from the group consisting of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate and mixtures thereof.

5. A composition as claimed in Claim 1, wherein said monomer is a member selected from the group consisting of polycaprolactone monoacrylate, ethylene glycol monomethyl ether acrylate, ethylene glycol monoethyl ether acrylate, ethylene glycol monobutyl acrylate, diethylene glycol monomethyl ether acrylate, diethylene glycol monoethyl ether acrylate, diethylene glycol monobutyl ether acrylate, phenyl glycidyl ether acrylate, phenoxyethyl acrylate, phenoxypropyl acrylate, phenoxypolyethylene glycol acrylate, phenoxypolypropylene glycol acrylate, monoacryloyloxyethyl phthalate, monoacryloyloxypropyl phthalate, monoacryloyloxyethyl tetrahydromethylphthalate, monoacryloyloxypropyl tetrahydromethylphthalate, dicyclopentanyl acrylate, dicyclopentenyl acrylate, dicyclopentenyl acrylate modified with ethylene oxide, isobornyl acrylate, monoacryloyloxyethyl phosphate, polycaprolactone monomethyacrylate, ethylene glycol monomethyl ether methacrylate, ethylene glycol monoethyl ether methacrylate, ethylene glycol monobutyl methacrylate, diethylene glycol monomethyl ether methacrylate, diethylene glycol monoethyl ether methacrylate, diethylene glycol monobutyl ether methacrylate, phenyl glycidyl ether methacrylate, phenoxyethyl methacrylate, phenoxypropyl methacrylate, phenoxypolyethylene glycol methacrylate, phenoxypolypropylene glycol methacrylate, monomethacryloyloxyethyl phthalate, monomethacryloyloxypropyl phthalate, monomethacryloyloxyethyl tetrahydromethylphthalate, monomethacryloyloxypropyl tetrahydromethylphthalate, dicyclopentanyl methacrylate, dicyclopentenyl methacrylate, dicyclopentenyl methacrylate modified with ethylene oxide, isobornyl methacrylate, monomethacryloyloxyethyl phosphate and mixtures thereof.

6. A composition as claimed in Claim 1, wherein said photopolymerization initiator is a member selected from the group consisting of benzoin alkyl ethers, acetophenone compounds, propiophenone compounds, anthraquinone compounds, thioxanthone, substituted thioxanthones, 1-hydroxycyclohexyl phenyl ketone and mixtures thereof.

7. A composition as claimed in Claim 1, wherein said photopolymerization initiator is a mixture of a benzoin compound of the following formula (I) with a priopiophenone compound of the following formula (II):

$$C_6H_5COCH(OR^1)C_6H_5 \qquad (I)$$

$$R^2\text{-}Z\text{-}COC(CH_3)_2OH \qquad (II)$$

wherein R^1 and R^2, independently from each other, stand for hydrogen or an alkyl and Z stands for 1,4-phenylene.

8. A composition as claimed in Claim 7, wherein R^1 stands for hydrogen or an alkyl having 1-4 carbon atoms and R^2 stands for hydrogen or an alkyl having 1-12 carbon atoms.

9. A composition as claimed in Claim 8, wherein R^1 stands for hydrogen, methyl, ethyl, n-propyl, i-propyl or n-butyl and R^2 stands for hydrogen, methyl, ethyl, n-propyl, isopropyl or n-hexyl.

10. A composition as claimed in Claim 1, wherein the amount of the ingredients (a)-(f) are as follows:

(a) 22-45 parts by weight;
(b) 22-35 parts by weight;
(c) 10-30 parts by weight;
(d) 12-35 parts by weight;
(e) 1-10 parts by weight; and
(f) 1-8 parts by weight.

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